Chemical improvement in paper making

The invention relates to an improvement in the printability of uncoated mechanical pulp paper grades, especially to an improvement in the printability of supercalendered (SC) papers, particularly in rotogravure printing. Objects of the invention are a method for improving the printability of uncoated mechanical pulp paper grades, the use of a combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer in said method, and paper prepared by said method.

Background of the invention

Mechanical pulp paper grades, or mechanical printing papers, comprise various newsprint grades, SC paper grades, and coated mechanical paper grades. Supercalendered (SC) papers contain 70-90% mechanical and/or recycled pulp and 10-30% chemical pulp and do not have any surface coating. Instead, they can contain up to 35% minerals as fillers, relative to the amount of fibrous raw materials which is marked as 100. Paper quality of SC papers is largely based on the quality of fibrous raw materials and fillers and their treatment and processing. Traditionally, printability properties of SC paper have been affected by including in the pulp such chemicals which provide the paper with strength (such as starch) and hydrophobicity (such as alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), styrene maleic anhydride (SMA)). Alternatively, the filler can be pretreated, for example to have a hydrophobic character.

In a calendering process, the web is passed through one or several nips for achieving the desired quality properties, especially as regards final thickness, gloss and smoothness. Supercalenders have a plurality of rolls arranged one above the other and nips provided between the rolls through which the paper web travels. A supercalender is usually arranged separately from the paper machine. It is also possible to calender the web 'on-line', which means that the calender is connected to the paper

machine. Before (super)calendering the web is usually wetted to a suitable calendering moisture by means of water and/or steam.

In US 6200424, an arrangement for calendering a board web is disclosed wherein a liquid containing a protein or a chemical that has properties similar to protein can be transferred on the board web via a moistening means before calendering. Alternatively, the moistening means are arranged so that the board web can be surface-sized and moistened simultaneously, or a coating containing a pigment can be transferred on the board web.

US 6494988 discloses a process for improving the surface of offset paper wherein a binding agent is applied across a moving paper web in a drying section or in a calender. In US 6500305, a process for on-line manufacture of SC-A paper (a subgrade within SC papers) is disclosed wherein tensides are added to the moistening water in order to produce a spray mist water having a reduced surface tension.

US 6013359 discloses different polyacrylamides as surface treatment agents for improving surface strength and releasing property of printing papers.

However, as far as the inventor is aware, in the earlier attempts to improve the printability of uncoated mechanical pulp paper grades, particularly SC papers, the chemicals used in the present invention have not been applied to the surface of the paper in connection with supercalendering to improve printability.

Different printing processes place different requirements on the quality and properties of the paper being printed. High-quality printing using a rotogravure process requires the paper surface to be smooth and at the same time little elastic, in order for the printing ink to settle properly on the paper. In rotogravure printing, printing pressure is the key factor in transferring ink to paper and this requires elasticity from the paper. Approximately 80% of SC papers is used in rotogravure printing, while 20% is used in offset printing. However, as the surface of SC papers has tradition-

ally not been treated with chemicals other than moistening water, high standards have been set for the supercalendering process in order to achieve the desired paper quality for printing, especially in case of rotogravure printing. Too strong and effective calendering can cause "blackening" (reduced brightness) of the paper which should be avoided. Supercalendering under high pressure and temperature also takes off bulkiness of paper which is not a desirable effect. Further, the porosity of SC papers should preferably be decreased, thus making the paper surface more dense, in order to improve the paper quality for printing purposes.

The rotogravure printing process is generally most suited to those applications in which a very large number of copies is required to be printed, because the process by which the surface of a rotogravure printing cylinder is prepared is expensive relative to the cost of preparing surfaces of printing cylinders for use in other methods of printing. A rotogravure printing cylinder has on its surface a matrix of cells or depressions which vary in depth according to the quantity of ink which is required to be transferred to the paper from each individual cell. Because of the large number of copies to be printed, it is generally advantageous to run the printing process at high speed.

Alkyl ketene dimer (AKD) and alkenyl succinic acid anhydride (ASA) are hydrophobing sizing agents used in internal and surface sizing of paper and paperboard under neutral or alkaline conditions. In surface sizing, AKD is used as a minor component together with starch (for example below 5%, often 1-3% by weight of starch), polyvinyl alcohol (PVA), carboxy methyl cellulose (CMC) or other polymer in liquid form. Structurally alkyl ketene dimers are unsaturated lactones. Technical grade saturated fatty acids, usually stearic acid, are used in the synthesis of AKD waxes. Prior to use, the waxes need to be converted into tiny particles dispersed in water by melting and emulsifying the wax. AKD sizes are usually provided in the form of anionic or cationic starch-stabilized dispersions.

Styrene maleic acid anhydride (SMA) is a copolymer of styrene and maleic acid anhydride. SMA-based hydrophobic surface sizing agents are used as additives in surface sizes to improve the hydrophobic properties of fine papers (woodfree papers), which contain no or very little mechanical pulp.

Summary of the invention

The present invention is based on the finding that the printability of uncoated mechanical pulp paper is improved by applying a combination of alkyl ketene dimer dispersion and styrene maleic acid anhydride copolymer solution onto the paper web, particularly before supercalendering.

Consequently, it is an object of the invention to provide a method for improving printability of uncoated mechanical pulp paper which method comprises applying a combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer onto at least one side of the paper web, preferably before supercalendering, and calendering the paper web.

A further object of the invention is the use of a combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer on paper surface for improving the printability of uncoated mechanical pulp paper grades.

Still another object of the invention is paper, preferably supercalendered paper or newsprint paper, prepared by a method wherein a combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer is applied onto the paper web in connection with, preferably before, calendering or supercalendering, and its use in a rotogravure printing process.

In a further, preferred embodiment of the invention, the above defined method is carried out by using any suitable application method, e.g. film transfer, blade, spray, moisturizing, or curtain application method.

Within this disclosure, by a "paper" is meant paper or paperboard or any material, preferably cellulosic material, which is suitable for printing. All weight ratios are calculated as dry weight and all percentages are percentages by weight.

Detailed description of the invention

The weight ratio of alkyl ketene dimer to styrene maleic acid anhydride copolymer in the combination to be applied onto the paper web as a mixture or separately is preferably about 1:1, but it may vary within the range 1:5 – 2:1. Usually the ratio of alkyl ketene dimer to styrene maleic acid anhydride copolymer is within the range of 1:1...2.

The styrene maleic acid anhydride copolymer is preferably provided as the ammonium salt form of SMA, for example as 10% aqueous solution. Also other salt forms of SMA, such as sodium, potassium, etc. are possible. The share of styrene in the styrene maleic acid anhydride copolymer is over 50%. The ratio of maleic acid anhydride units to styrene units is generally in the range of from 10:90 to 45:55, preferably 20:80 – 40:60. Especially suitable are styrene maleic acid anhydride copolymers having a molecular weight from 5000 to 500 000. The styrene maleic acid anhydride copolymer is prepared in a known manner, for example by polymerizing the monomers in organic solution.

The alkyl ketene dimer can be supplied as an aqueous dispersion which usually contains starch or another polymer in liquid form as stabiliser. The AKD content of said dispersion may be for example from 60 to 95%. Alkyl ketene dimers with a melting point within the range of 15-70°C are suitable. Especially preferred is a mixture of low melting (<30°C) and high melting (>50°C) alkyl ketene dimers, wherein for example <30% of alkyl ketene dimers are low melting and >70% high melting alkyl ketene dimers. Starch or other polymer in liquid form may be used as a protective

colloid to stabilize the dispersion in an amount of 5-40% of the total dispersion, especially in an amount of 10-20%.

The combination of alkyl ketene dimer and styrene maleic acid anhydride can be applied onto the paper web as a mixture or as two separate dispersions. The mixture of alkyl ketene dimer and styrene maleic acid anhydride copolymer is a dispersion with a dry matter content of 5-15%. If the two chemicals are applied separately, AKD may be applied as an AKD dispersion (for example as 18% dispersion) and SMA as a SMA solution (for example as 10% solution), one after the other.

Preferably the combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer is applied onto the paper web before calendering. Calendering may take place either "on-line" at the paper machine or at a separate calendering unit. The combination of AKD and SMA can be applied onto the web at a separate (super)calender before or during calendering, or at the paper machine before or during on-line (super)calendering. Another alternative is to apply the combination of AKD and SMA at the (dry end of) paper machine and then pass the web to a separate (super)calender. Before applying the combination of AKD and SMA, the web can be dried to a suitable moisture content, which is preferably <20%, more preferably <15%.

A further embodiment of the invention is to apply a mixture of alkyl ketene dimer and styrene maleic acid anhydride copolymer onto the paper web together with moistening water before or during calendering. In a still further embodiment the mixture is applied onto the wet or dry web, the web is possibly dried to desired moisture, and then the web is passed to a calender, preferably to a supercalender. It is also possible to apply the mixture onto paper which has already been calendered, before an additional (super)calendering. In the recently developed new calendering units it may also be possible to apply the mixture in between two stacks of calender rolls.

The application methods such as curtain application and spray application which have recently become more general, make it also possible to apply AKD and SMA one after another. In this embodiment according to the invention, AKD is preferably applied first, as SMA is a better film forming agent than AKD.

A person skilled in the art understands that a combination of AKD and SMA, especially their mixture, improves the printability of uncoated mechanical pulp paper even if the paper web is not (super)calendered after applying the combination of AKD and SMA to the web. However, the paper web may, if desired, be calendered before the combination of AKD and SMA is applied on the web.

Further, if desired, known paper quality improving agents, such as optical brighteners, pH regulators, lubricating agents, etc. may be added together or separately with the combination of alkyl ketene dimer and styrene maleic acid anhydride. However, in the method according to the invention no pigments, latexes, nor polymers like starch, PVA or CMC (except the polymers possibly included in AKD dispersion) are applied onto the paper web.

The combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer is applied onto the paper web in an amount which is less than or about 1 g/m^2, preferably about 0.5 g/m^2, or from 0.05 to 0.8 g/m^2.

Applying the combination of alkyl ketene dimer and styrene maleic acid anhydride copolymer onto the paper web in connection with calendering or supercalendering improves the printability properties of the (super)calendered paper. The paper surface becomes more hydrophobic, smoother, and has improved gloss properties compared to usual SC papers. The porosity of the paper surface is reduced and the surface is more dense, as the application of AKD and SMA forms a thin film on the paper surface. The high-quality paper obtained by the method of the invention is particularly suitable for rotogravure printing, being fully competitive with pigment-coated papers.

A further advantage of the use of a combination of alkyl ketene dimer and styrene maleic anhydride is that there is no need for "over-effective" calendering, which means that no blackening effect appears and the bulkiness of paper is not decreased.

The following examples further illustrate the invention.

Example 1

Uncalendered mechanical base paper was processed with different chemicals so that applied weight was about 0.5 g/m^2. The paper was calendered in a laboratory calender in paper moisture of 9.5% under pressure of 50 bar and at a temperature of 90°C. The calendered paper was tested for printability in rotogravure printing.

The chemicals used were water, alkyl ketene dimer (AKD) dispersion, styrene maleic anhydride copolymer (SMA) solution, polyethylene glycol (PEG) and a mixture of AKD and SMA. The SMA copolymer contained 28% maleic acid anhydride and 72% styrene. The AKD dispersion was a mixture of low melting (20%) and high melting (80%) alkyl ketene dimers. Commercial SC paper was used as a reference. Styrene acrylate latex was also tested but it stuck tightly on the calender roll and could not be analysed.

Table 1.

	print density	printed gloss	Heliotest
reference	1.72	71	54
water	1.76	72	62
AKD	1.76	71	110
SMA	1.80	69	42
AKD+SMA	1.82	73	110
PEG	1.76	71	34

In the Heliotest, missing dots are inevitable at 5% half tone but disastrous when occurring at 20% and 30% half tones. The number of missing dots is a traditional measure of rotogravure printability of paper. In laboratory printing, the so-called

Heliotest indicates the number of missing dots. The Heliotest fitting developed by Centre Technique du Papier is used here with an IGT AC2 laboratory printer. The test figure is 110 mm long with an 8 mm wide raster where the tone changes from dark to light. The size of the dots is constant over the entire printing area. The number of missing dots is defined as a distance from the dark end of the printed image within which 20 missing dots can be detected. The longer the distance the better the rotogravure printability of the paper. A dot where more than half of the dot area is missing is considered as a missing dot.

From the results it can be seen that the mixture of alkyl ketene dimer and styrene maleic anhydride copolymer gives better density than other chemicals tested. Printed gloss is also better and in Heliotest there is a big difference in relation to missing dots.

Example 2

The surface of usual SC paper was processed with different chemicals to about 0.5 g/m^2. The paper was calendered in a moisture of 5.5%. The temperature was 90°C and a pressure of 40 bar was used. The calendered paper was tested for printability in rotogravure printing. Reference was usual SC paper.

Table 2.

	print density	printed gloss	Heliotest
reference	1.74	73	52
water	1.78	75	56
AKD	1.78	76	95
SMA	1.91	77	34
AKD+SMA	1.91	79	110

The mixture of AKD and SMA provides better print density and printed gloss than the reference or water processed SC paper. Heliotest is clearly better in missing dots appearance. Especially the printed gloss achieved by using a mixture of alkyl ketene dimer and styrene maleic acid anhydride as described in this invention is better than

that achieved by any of its components alone. Polyethylene glycol (PEG) was not used because it adhered to calender roll.